REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
28/03/2012

2. REPORT TYPE
28/03/2012

3. DATES COVERED *(From - To)*
06/15/2008 - 12/14/2011

4. TITLE AND SUBTITLE
HEALABLE COMPOSITES

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-08-1-0314

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Professor Siavouche (Sia) Nemat-Nasser,
Center of Excellence for Advanced Materials [CEAM], UC San Diego

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of California, San Diego
Office of Contracts and Grant Administration
9500 Gilman Drive Dept 621

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St.
Arlington, VA 22203
Dr. Byung Lee/RSA

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-OSR-VA-TR-2012-1142

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION A: APPROVED FOR PUBLIC RELEASE

13. SUPPLEMENTARY NOTES

14. ABSTRACT
This research on healable polymers and composites has led to the development of experimental and computational characterization tools, novel fabrication methods, and collaborative partnerships with other researchers. We worked to synthesize the monomers necessary to create the healable polymer. A new synthesis route was identified and implemented for producing the furan monomer, 4FS. The new route is faster and has a higher yield than the previous method. Tens of grams of both monomers (4FS and 2MEP) were produced at higher purities than during previous work at CEAM. Polymerizing the two monomers creates the healable polymer 2MEP4FS. The presence of the thermally reversible Diels-Alder cross-linking adducts in this polymer was confirmed using differential scanning calorimetry (DSC). The polymer was tested with dynamic mechanical analysis (DMA) and exhibited a small increase in the storage modulus and glass transition temperature over previous 2MEP4FS results. A new monomer, 3FT, was also developed in an effort to increase the glass transition temperature of the healable polymer, but no thermally reversible reactions

15. SUBJECT TERMS
Healable Composites

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	U	36	19b. TELEPHONE NUMBER *(Include area code)*

Reset

INSTRUCTIONS FOR COMPLETING SF 298

1. REPORT DATE. Full publication date, including day, month, if available. Must cite at least the year and be Year 2000 compliant, e.g. 30-06-1998; xx-06-1998; xx-xx-1998.

2. REPORT TYPE. State the type of report, such as final, technical, interim, memorandum, master's thesis, progress, quarterly, research, special, group study, etc.

3. DATES COVERED. Indicate the time during which the work was performed and the report was written, e.g., Jun 1997 - Jun 1998; 1-10 Jun 1996; May - Nov 1998; Nov 1998.

4. TITLE. Enter title and subtitle with volume number and part number, if applicable. On classified documents, enter the title classification in parentheses.

5a. CONTRACT NUMBER. Enter all contract numbers as they appear in the report, e.g. F33615-86-C-5169.

5b. GRANT NUMBER. Enter all grant numbers as they appear in the report, e.g. AFOSR-82-1234.

5c. PROGRAM ELEMENT NUMBER. Enter all program element numbers as they appear in the report, e.g. 61101A.

5d. PROJECT NUMBER. Enter all project numbers as they appear in the report, e.g. 1F665702D1257; ILIR.

5e. TASK NUMBER. Enter all task numbers as they appear in the report, e.g. 05; RF0330201; T4112.

5f. WORK UNIT NUMBER. Enter all work unit numbers as they appear in the report, e.g. 001; AFAPL30480105.

6. AUTHOR(S). Enter name(s) of person(s) responsible for writing the report, performing the research, or credited with the content of the report. The form of entry is the last name, first name, middle initial, and additional qualifiers separated by commas, e.g. Smith, Richard, J, Jr.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES). Self-explanatory.

8. PERFORMING ORGANIZATION REPORT NUMBER. Enter all unique alphanumeric report numbers assigned by the performing organization, e.g. BRL-1234; AFWL-TR-85-4017-Vol-21-PT-2.

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES). Enter the name and address of the organization(s) financially responsible for and monitoring the work.

10. SPONSOR/MONITOR'S ACRONYM(S). Enter, if available, e.g. BRL, ARDEC, NADC.

11. SPONSOR/MONITOR'S REPORT NUMBER(S). Enter report number as assigned by the sponsoring/ monitoring agency, if available, e.g. BRL-TR-829; -215.

12. DISTRIBUTION/AVAILABILITY STATEMENT. Use agency-mandated availability statements to indicate the public availability or distribution limitations of the report. If additional limitations/ restrictions or special markings are indicated, follow agency authorization procedures, e.g. RD/FRD, PROPIN, ITAR, etc. Include copyright information.

13. SUPPLEMENTARY NOTES. Enter information not included elsewhere such as: prepared in cooperation with; translation of; report supersedes; old edition number, etc.

14. ABSTRACT. A brief (approximately 200 words) factual summary of the most significant information.

15. SUBJECT TERMS. Key words or phrases identifying major concepts in the report.

16. SECURITY CLASSIFICATION. Enter security classification in accordance with security classification regulations, e.g. U, C, S, etc. If this form contains classified information, stamp classification level on the top and bottom of this page.

17. LIMITATION OF ABSTRACT. This block must be completed to assign a distribution limitation to the abstract. Enter UU (Unclassified Unlimited) or SAR (Same as Report). An entry in this block is necessary if the abstract is to be limited.

AFOSR 'FINAL' TECHNICAL REPORT

Grant/Contract Title: HEALABLE COMPOSITES
Grant No: FA9550-08-1-0314
Period of Performance: June 15, 2008 – December 14, 2011

PI: Sia Nemat-Nasser,
Center of Excellence for Advanced Materials [CEAM], UC San Diego

AFOSR Program Manager: Dr. Byung-Lip Lee

Report Submitted [March 28, 2012] via http//afosr.reports.sgizmo.com/s3. The full report [including ppt's] was also submitted to technicalreports@afosr.af.mil

****

I. SCIENTIFIC PERSONNEL [supported directly or indirectly]:

Christian Nielsen (project start to 12/14/11) – CEAM Graduate Student Researcher – Characterized healable polymers with thermally reversible cross-linking bonds; developed healable fiber reinforced composites, and studied the double cleavage drilled compression (DCDC) fracture test.

Dr. Alireza V. Amirkhizi (project start to 12/14/11) – CEAM Research Scientist – Computational and theoretical modeling of the DCDC [double cleavage drilled compression] experiment.

Prof. Haim Weizman (September 2008 to September 2011) – UCSD Dept. of Chem/Biochem – Synthesizing of monomers and developing new/modified components including functionalized glass particles.

Or Weizman (June 2008 to July 2010) – CEAM High-School Intern/Volunteer – Assisted with synthesis of the first batch of monomers; studied monomers/polymer using DSC [differential scanning calorimetry]; fabricated a fiber-reinforced healable composite using a solvent-based approach.

Dmitry Uchenik (March 2010 to June 2010) – Previous UCSD undergraduate chemistry student working with Prof. Weizman to synthesize monomers.

Eva Baylon (January 2009 to September 2009) – undergraduate student [McNair scholar] – conducted research as part of the McNair program. Winter quarter: literature study on healable materials and the DCDC tests. Spring quarter: studied the effect of polymerization time and temperature on the quality of the resulting material. Summer quarter: conducted DCDC tests on polymers.

Prof. Yitzhak Tor (September 2008 to Sept 2011) – UCSD Dept. of Chem/Biochem – Chemistry consultation.

II. PARTICIPATION IN CONFERENCES/SYMPOSIA:

March, 2009: SPIE 2009 International Symposium on Smart Structures and Materials, "Constructing Effective Healable Polymer Composites," presented by Christian Nielsen, UCSD, San Diego, CA.

June 1-4, 2009. SEM 2009 Annual Conference, "Geometric Effects in DCDC Fracture Experiments, " presented by Alireza V. Amirkhizi, Albuquerque, NM.

June 30, 2009. Second International Conference on Self-Healing Materials, "Healable Polymers: Characterization", presented by Sia Nemat-Nasser, Chicago, IL.

March 7-11, 2010: SPIE 2010 International Symposium on Smart Structures and Materials: Active Polymers I, "Characterization of healable polymers", presented by Christian Nielsen, San Diego, CA.

June 7-10, 2010: SEM 2010 Annual Conference: Fracture of Polymers and Adhesives, "Thermal and Mechanical Characterization of a Healable Polymer," presented by Christian Nielsen, Indianapolis, IN.

March 6-10, 2011: SPIE 2011 International Symposium on Smart Structures and Materials: Behavior and Mechanics of Multifunctional Materials and Composites V, "Fabrication of Fibrous Composites with Re-mendable Polymer Matrices", Poster presented by Christian Nielsen, San Diego, CA.

June 13-16, 2011: SEM 2011 Annual Conference: General Fracture and Fatigue II, "The Influence of Sample Thickness on the DCDC Fracture Test," presented by Christian Nielsen, Uncasville, CT.

June 13-16, 2011: SEM 2011 Annual Conference: Interfaces, Interphases, Inhomogeneities I, "Using Remendable Polymers for Aerospace Composite Structures," presented by Dr. Terrisa Duenas [NextGen Aero], Uncasville, CT.

III. ACCOMPLISHMENTS:

This research on healable polymers and composites has led to the development of experimental and computational characterization tools, novel fabrication methods, and collaborative partnerships with other researchers.

We worked with the UCSD Department of Chemistry to synthesize the monomers necessary to create the healable polymer. A new synthesis route was identified and implemented for producing the furan monomer, 4FS. The new route is faster and has a higher yield than the previous method. Tens of grams of both monomers (4FS and 2MEP) were produced at higher purities than during previous work at CEAM. Polymerizing the two monomers creates the healable polymer 2MEP4FS. The presence of the thermally reversible Diels-Alder cross-linking adducts in this polymer was confirmed using differential scanning calorimetry (DSC). The polymer was tested with dynamic mechanical analysis (DMA) and exhibited a small increase in the storage modulus and glass transition temperature over previous 2MEP4FS results. A new monomer, 3FT, was also developed in an effort to increase the glass transition temperature of the healable polymer, but no thermally reversible reactions were observed during testing.

In a paper published in the *Journal of Chemical Education*, we outlined a set of experiments for an undergraduate chemistry lab. The students synthesize 4FS and polymerize it with a commercially available bismaleimide to create a healable polymer. Thermally reversible bonding is observed using DSC, and healing is demonstrated in a thin film of the polymer. The lab illustrates how a molecular level reaction mechanism (the Diels-Alder adduct) can have useful macro-level implications (healing).

Research has been conducted on the double cleavage drilled compression (DCDC) fracture test. The effect of sample thickness and hole size was studied using poly(methyl methacrylate) (PMMA). A computational model for estimating a critical stress intensity factor (KIc) from DCDC data was also developed. PMMA was estimated to have a K_{Ic} in the range of 0.6 to 0.75 MPa·m$^{1/2}$. 2MEP4FS created using the new, more efficient synthesis route was estimated to have a K_{Ic} in the range of 0.5 to 0.6 MPa·m$^{1/2}$, a 17% increase over previous 2MEP4FS DCDC results.

Multilayered healable composites were fabricated using a pre-preg process. A solvent-based approach was unsuccessful as the solvent reduced the modulus and glass transition temperature of the final material. An alternative approach was developed where the 2MEP4FS prepolymer temperature was modulated to control the polymerization rate. A stoichiometric ratio of 2MEP and 4FS monomers was partially polymerized at elevated temperatures before being quenched to slow the reaction. The resulting prepolymer was integrated with a unidirectional layer of carbon fiber. Four pre-preg layers were stacked in a [90,0,0,90] orientation, and the polymerization was completed with heat and pressure. The resulting sample was characterized using DMA before and after fracturing and healing thermal treatments. The sample exhibited a 44% healing efficiency.

We investigated functionalizing glass fibers to create a composite material with a healable matrix and healable matrix-fiber interface. We functionalized milled glass fibers with amino groups as a preliminary step to functionalizing the fibers with groups that will create Diels-Alder adducts with a polymer matrix.

Mr. Christian Nielsen [graduate student] collaborated via teleconferences with NextGen Aeronautics during the period of September 2009 to June 2011. Christian characterized a

single component healable polymer [material provided by NextGen, and previously developed in Prof. Fred Wudl's lab at UCLA]. With a limited supply of monomer available, Christian was able to obtain useful information from DSC thermal tests and polymerization studies.

IV. PUBLICATIONS IN ARCHIVAL JOURNALS AND CONFERENCE PROCEEDINGS

Nielsen, C., A.V. Amirkhizi, S. Nemat-Nasser. "The Influence of Sample Thickness on the DCDC Fracture Test." *Proceedings of the 2011 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, Uncasville, CT, June 13-16, 2011 [2011] 3 pages. [Extended abstract].

Abstract: The double cleavage drilled compression (DCDC) fracture test uses axial compression to drive stable cracks in glasses and brittle polymers. The cracks are generated by regions of tension in a rectangular column of material containing a central hole. The observed relationship between crack length and the applied axial stress is fitted with a two-dimensional finite element model to estimate fracture toughness. The model is applied to previous DCDC experimental results for poly(methyl methacrylate) (PMMA) samples of varying thicknesses. Both plane stress and plane strain cases are considered. Three dimensional finite element models of the DCDC test indicate plane stress analysis is the most applicable condition and suggest explanations for the effect of sample thickness.

Weizman, H., C. Nielsen, O.S. Weizman, S. Nemat-Nasser. "Synthesis of a Self-Healing Polymer Based on Reversible Diels–Alder Reaction: An Advanced Undergraduate Laboratory at the Interface of Organic Chemistry and Materials Science." *Journal of Chemical Education*, Vol. 88 [2011] 1137-1140.

Abstract: This laboratory experiment exposes students to the chemistry of self-healing polymers based on a Diels–Alder reaction. Students accomplish a multistep synthesis of a monomer building block and then polymerize it to form a cross-linked polymer. The healing capability of the polymer is verified by differential scanning calorimetry (DSC) experiments. Furthermore, healing is demonstrated by damaging and heat-treating a thin polymer film.

Nielsen, C., H. Weizman and S. Nemat-Nasser, "Thermal and Mechanical Characterization of a Healable Polymer," *SEM Annual Conference and Exposition on Experimental and Applied Mechanics*, June 7-10, 2010, Indianapolis, IN, ISBN: 978-1-935116-05-9 (2010) 3 pages. [Extended abstract].

Abstract: A cross-linked polymer capable of reforming broken bonds is considered a healable polymer. One such polymer, 2MEP4FS, has previously been shown to regain full toughness under ideal fracture and healing conditions. Here, a more purified 2MEP4FS polymer is characterized using thermal and mechanical techniques and compared with the previous 2MEP4FS polymer. Modulated differential scanning calorimetry (MDSC) confirms the presence of the thermally reversible Diels-Alder bonds necessary for healing. Dynamic mechanical thermal analysis (DMTA) establishes mechanical properties and the glass

transition temperature. Fracture and healing tests are conducted using the double cleavage drilled compression (DCDC) geometry. Compression drives symmetric cracks up and down a rectangular column of material with a central through-thickness hole. Correlating the applied stresses and crack lengths with a finite element model, critical stress intensity factors are estimated. The cracks are healed with a thermal treatment and light pressure, and the sample is retested. Over the course of multiple fracture and healing cycles, changes in the critical stress intensity factor are used to establish a healing efficiency.

Nielsen, C., O. Weizman and S. Nemat-Nasser, "Characterization of Healable Polymers," ***Proceedings of Behavior and Mechanics of Multifunctional Materials and Composites 2010,*** **SPIE's 17th Annual International Conference on Smart Structures and Materials, Vol. 7644 (2010) 76441B-1-76441B-4. AFOSR FA9550-08-1-0314 to UC San Diego.**

Abstract: Materials with an internal mechanism for damage repair would be valuable in isolated environments where access is difficult or impossible. To this end, a fibrous composite structure is envisioned with a healable polymer matrix. Current work is focused on characterizing neat polymers with reformable cross-linking bonds. These bonds are thermally reversible, the result of a Diels-Alder cycloaddition between furan and maleimide monomers. Candidate polymers are examined using modulated differential scanning calorimetry (MDSC) to confirm the presence of reversible bonding. One polymer, 2MEP3FT, was expected to have these bonds, but none were observed. A second polymer, 2MEP4FS, with a modified furan monomer does exhibit reversible bonding. Further MDSC testing and dynamic mechanical thermal analyses (DMTA) are conducted to determine material properties such as glass transition temperature, Young's modulus and quality of the polymerization. Healing efficiency is established using the double cleavage drilled compression (DCDC) fracture test. A column of material with a central hole is subjected to axial compression, which drives cracks up and down the sample. Removing the load allows the crack faces to come together, a necessary condition for the reestablishment of broken bonds. This healing process is accelerated with a heat treatment. By retesting the sample, a healing efficiency of the polymer is determined. The effect of multiple fracture/healing cycles on the healing efficiency of the polymer is considered.

Nielsen, C., A.V. Amirkhizi and S. Nemat-Nasser, "Geometric Effects in DCDC Fracture Experiments," ***Proceedings of 2009 SEM Annual Conference and Exposition on Experimental and Applied Mechanics*****, June 1-4, 2009, Albuquerque, NM, ISBN: 978-1-935116-03-5 (2009) 3 pages [Extended abstract].**

Abstract: The effect of sample geometry on the double cleavage drilled compression (DCDC) test of PMMA is experimentally and numerically studied. The test uses axial compression to propagate cracks in a rectangular column of material containing a central circular hole. Initiated by notches, the cracks grow slowly at first with increasing load then more rapidly before being arrested due to the confined end conditions. Specific geometric parameters considered in this study are the sample thickness and hole size. Tested

thicknesses include 3, 4, 5, 8, and 11 mm (all at 50 mm height and 12 mm width). The thin samples (3, 4 and 5 mm) are tested in a brace to prevent out-of-plane buckling. Width-to-hole-diameter ratios of 4 and 6 are investigated. The results of these experiments are incorporated in numerical simulations to estimate the fracture toughness of the material. Measured loads are matched with numerical models of different crack lengths to estimate energy release rates and critical stress intensity factors. The simulations consider nonlinear geometric effects. The knowledge from this work will be applied to future DCDC tests of re-mendable polymers, where repeated cycles of fracture and healing will determine healing efficiency.

Nielsen, C., H. Weizman, S. Nemat-Nasser. "Healable Polymers: Characterization." ***Proceedings of Second International Conference on Self-Healing Materials 2009*****, Chicago, IL, June 28-July 1, 2009. [extended abstract]**

Abstract: Re-mendable polymer 2MEP4FS derived from a Diels-Alder (DA) reaction has previously been studied. DA bonding between the maleimide and furan monomers provides a high degree of cross-linking, but unlike traditional highly cross-linked polymers, thermally reversible DA bonds can be re-established after fracture. Fracture tests of 2MEP4FS have shown the material can completely regain its resistance to fracture, even after multiple repairs. Although it has mechanical properties comparable with epoxy (4.7 GPa elastic modulus), the 93 °C glass transition temperature is relatively low, and synthesis of the furan is difficult and time consuming. A polymer with similar healing capabilities and mechanical characteristics, but improved thermal properties that is easier to manufacture is highly desirable. In the present work, a new furan monomer, 3FT, is polymerized with 2MEP to create 2MEP3FT polymer. 3FT consists of three furan groups bonded to a central 1,3,5 triazine ring, a design that can be quickly synthesized. The resulting 2MEP3FT polymer is expected to have a higher stiffness than 2MEP4FS. Initial modulated differential scanning calorimetry (MDSC) results indicate a significantly higher glass transition temperature, in excess of 120 °C. Further MDSC and dynamic mechanical analysis (DMA) testing will be presented.

Nielsen, C., A.V. Amirkhizi, S. Nemat-Nasser. "The Effect of Geometry on Fracture Strength Measurement Using DCDC Samples," ***Engineering Fracture Mechanics*** **[SUBMITTED 10/2011]**

Abstract: The fracture behavior of poly (methyl methacrylate) (PMMA) is studied using double cleavage drilled compression (DCDC) experiments. These experiments employ axial compression to drive stable tension cracks in a material. Increasing specimen thickness is found to increase the stresses required to propagate long cracks. Crack surface features show a correlation with regimes and speeds of crack growth. Decreasing hole size led to significant inelastic deformation during testing, and, after unloading, the formation of new stress-relieving cracks at the hole edges, normal to the loading direction. A computational model is developed to estimate energy release rates and critical stress intensity factors, based on experimental data. The model gives the critical stress intensity factor of PMMA to be 0.6 to 0.75 $MPa \cdot m^{1/2}$. Photoelastic observations are used to compare experimentally observed and simulated stress distributions.

V. CHANGES IN RESEARCH OBJECTIVES (IF ANY): None

VI. TECHNICAL RESEARCH REPORT: SEE ATTACHED

Power-point Presentation “Healable Composites” Presented by Mr. Christian Nielsen, 2011 AFOSR Annual Grantees’/Contractors Meeting in Arlington VA, August 1-5, 2011.

Healable Composites

Sia Nemat-Nasser (PI)

Christian Nielsen (Graduate Student)

AFOSR Annual Grantees'/Contractors' Meeting
Mechanics of Multifunctional Materials & Microsystems

August 2, 2011

UCSD
CENTER OF EXCELLENCE FOR
ADVANCED MATERIALS

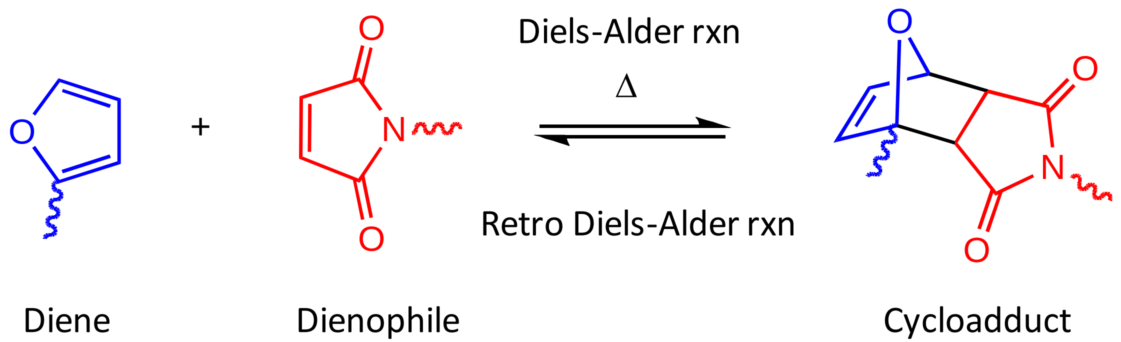
Overview

- Background
- Research Outline
- Monomers
- Polymer
- Composite

Motivation

- How to repair inaccessible structures?
  - Design structure using a 'healable' material with an internal mechanism for repairing damage

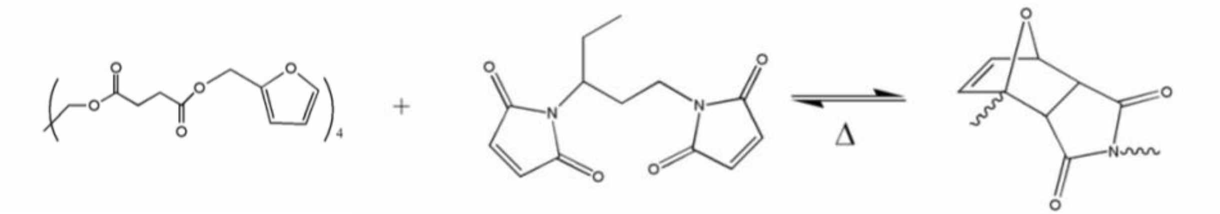
Fibrous composite with a reversibly cross-linked polymer matrix:



Exploit cross-link reversibility for healing

Previous Work

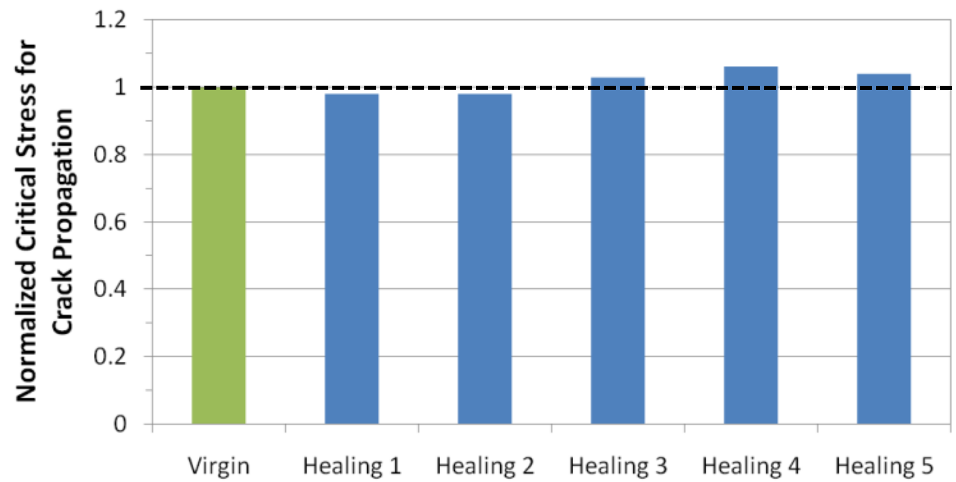
- Diels-Alder-based polymer 2MEP4FS



4FS tetrafuran　　2MEP bismaleimide　　2MEP4FS

Chen X, Wudl F et al, New thermally remendable highly cross-linked polymeric materials, Macromolecules 36 (2003)

- Mechanical testing of 2MEP4FS at CEAM

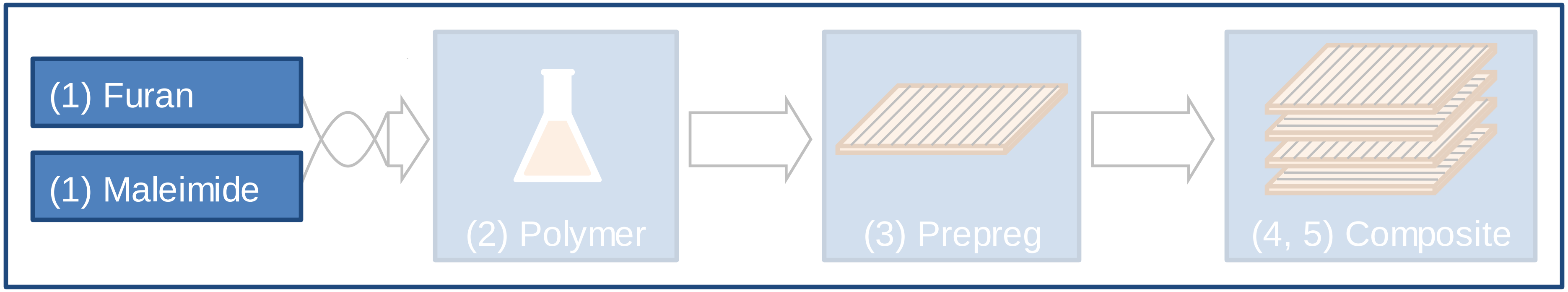


→ Material *completely* regains its resistance to fracture

Plaisted T, Nemat-Nasser S, Quantitative evaluation of fracture of reversibly cross-linked polymer, Acta Materialia 55 (2007).

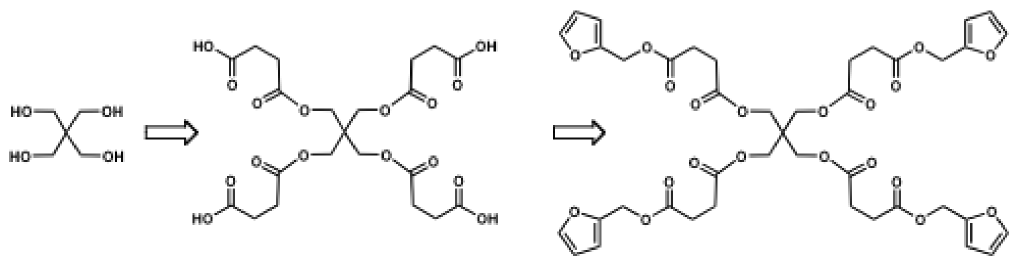
Research Outline

1. Process polymer components: furan and maleimide monomers
2. Characterize neat polymer (mechanical, thermal and crack healing properties)
3. Develop pre-preg system of oriented fibers and healable polymer matrix
4. Laminate pre-preg layers to form composite panels with minimal voids & defects
5. Characterize the composites: determine mechanical and crack healing properties

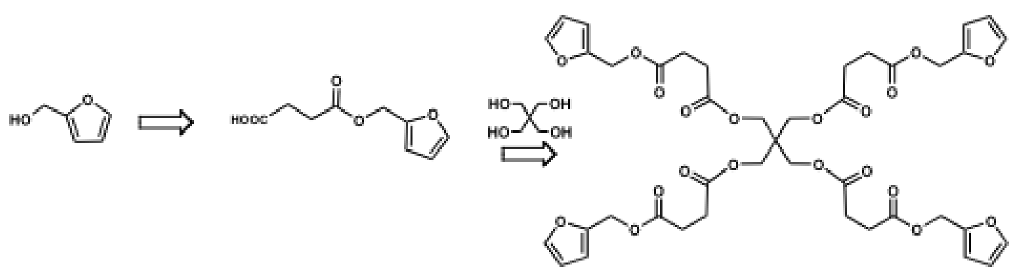


Monomer Synthesis

- 2MEP bismaleimide synthesized according to **established** procedure
- 4FS tetrafuran procedure **modified**
  - Previous method: linear synthesis



  - Modified method: **convergent** synthesis



↘ Collaboration with UCSD Department of Chemistry:

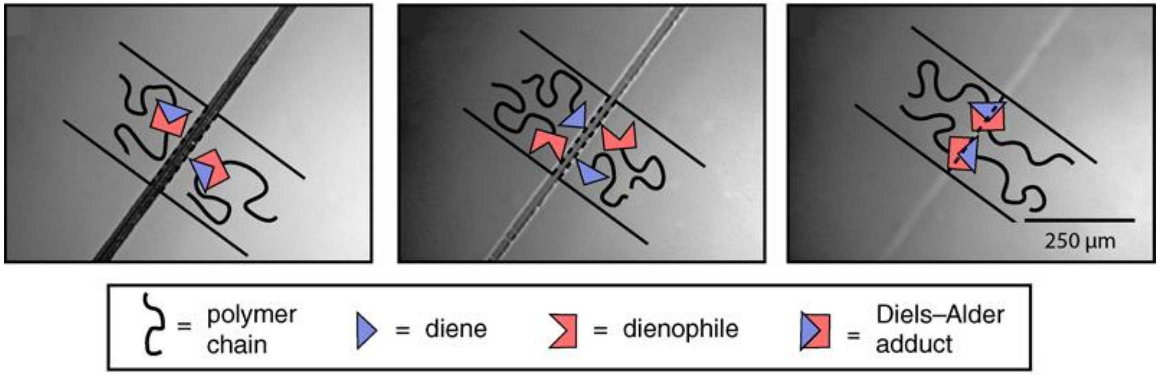
Prof. Haim Weizman
Dmitriy Uchenik

Modified method has a *higher* yield and is *easier* to purify

Healable Polymers as a Teaching Tool

Synthesis of a Self-Healing Polymer Based on Reversible Diels-Alder Reaction: An Advanced Undergraduate Laboratory at the Interface of Organic Chemistry and Materials Science

H. Weizman, C. Nielsen, O.S. Weizman, and S. Nemat-Nasser
J Chem Ed 88(8), p. 1137-1140, 2011



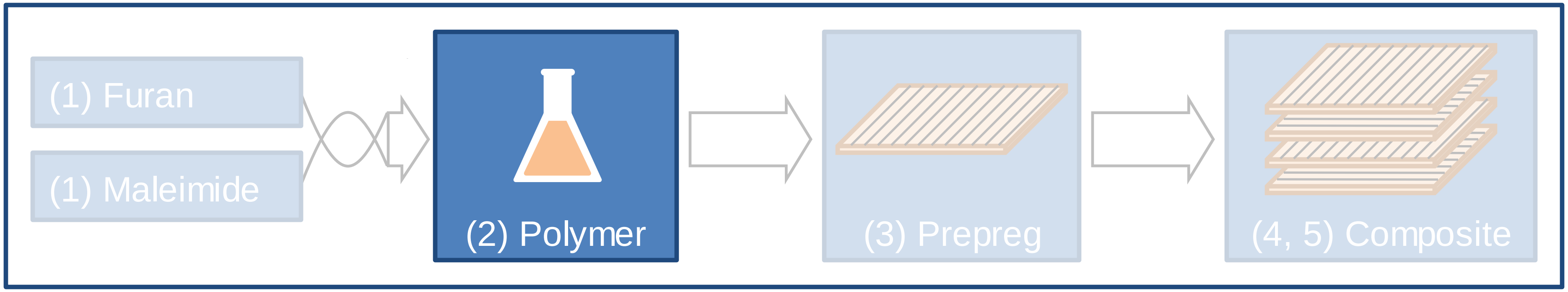
Lab Objectives:

- Synthesize 4FS
- Create polymer
- Demonstrate healing

Students learn how a reaction mechanism at the **molecular level** can translate to a useful **macro-level** phenomenon

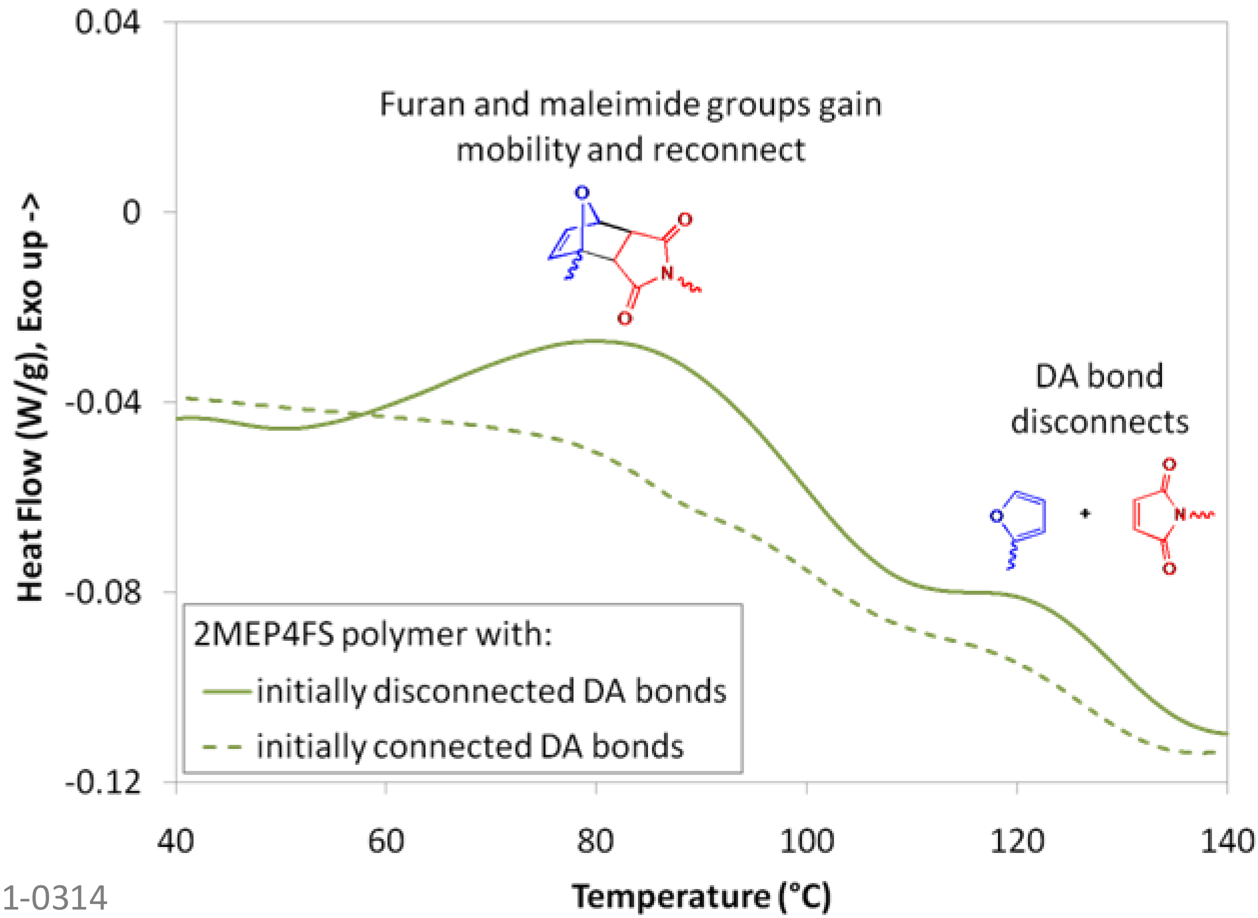
Research Outline

1. Process polymer components: furan and maleimide monomers
2. Characterize neat polymer (mechanical, thermal and crack healing properties)
3. Develop pre-preg system of oriented fibers and healable polymer matrix
4. Laminate pre-preg layers to form composite panels with minimal voids & defects
5. Characterize the composites: determine mechanical and crack healing properties



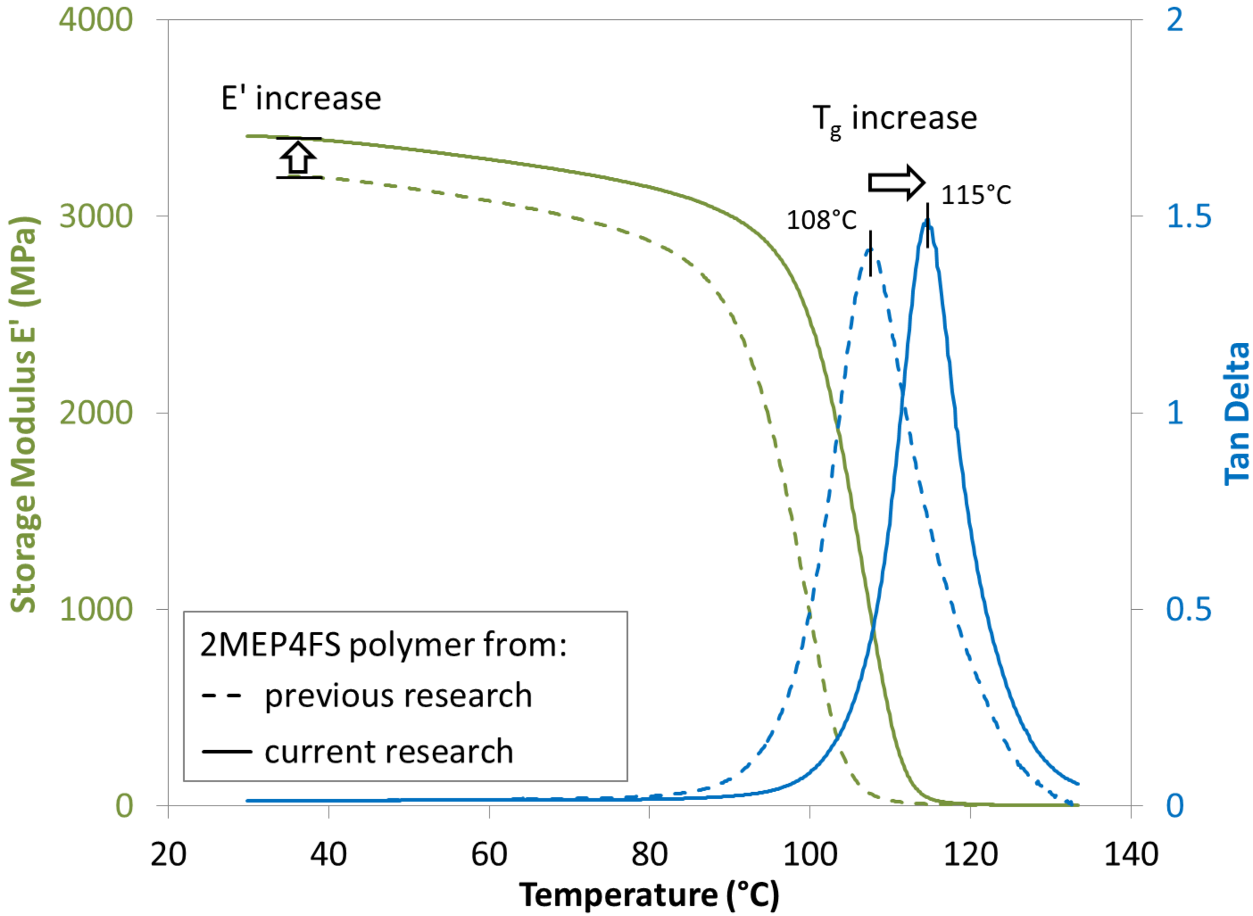
DSC Testing

- Differential scanning calorimetry (DSC) confirms the presence of **thermally reversible bonds** in 2MEP4FS



DMA Testing

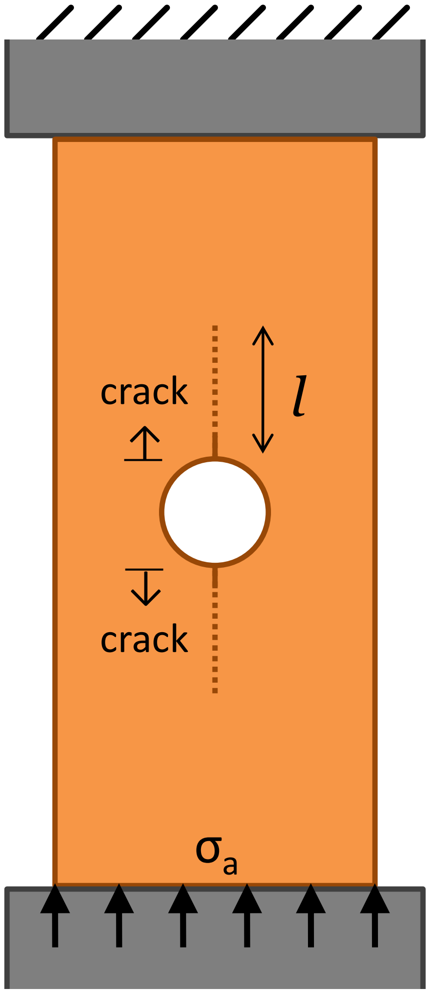
- Dynamic mechanical analysis indicates new synthesis method has **increased 2MEP4FS *E'*, T_g**



Fracture Testing

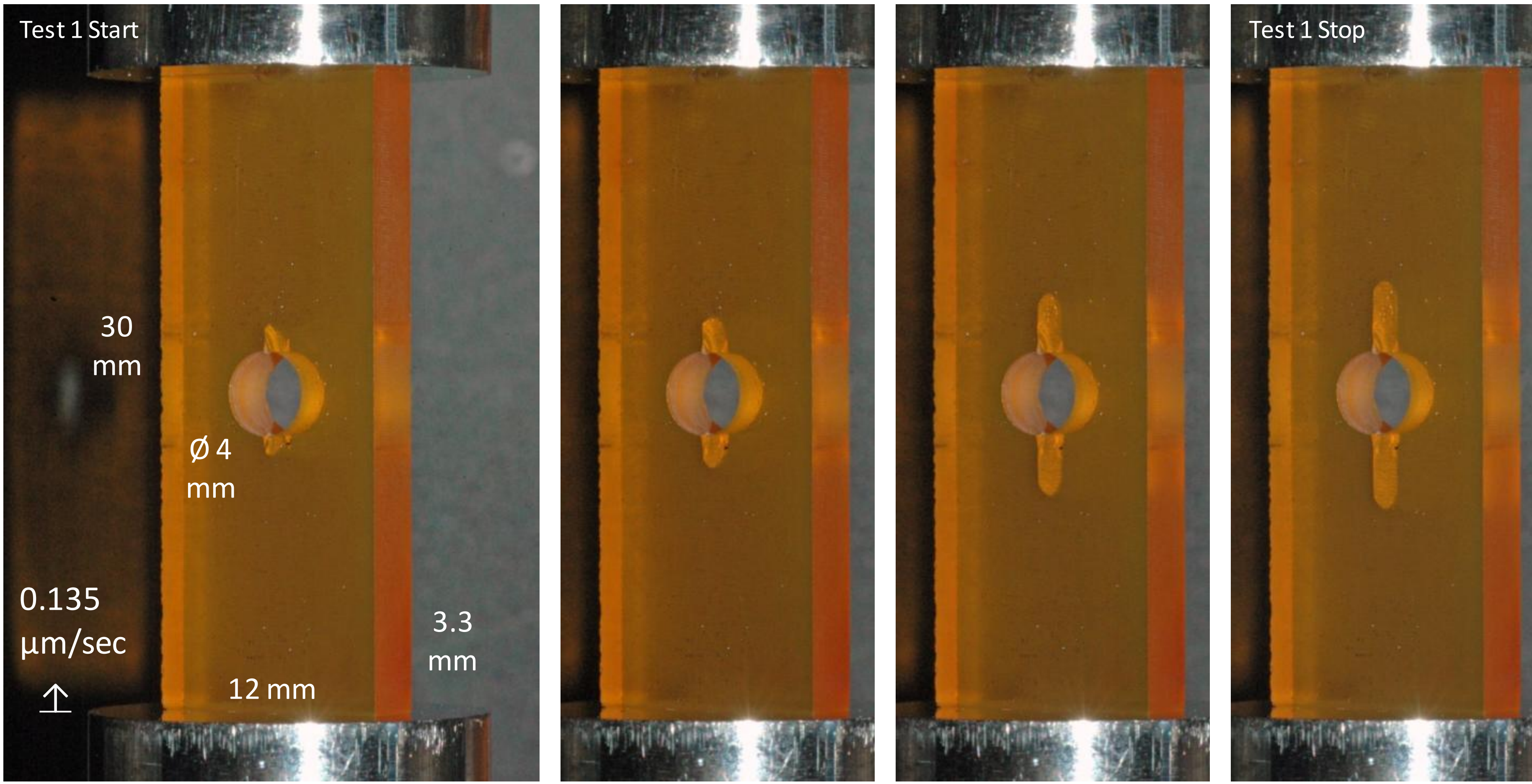
- Double cleavage drilled compression (DCDC) sample geometry
  - Use compression to drive tension cracks
  - Examine crack propagation behavior (i.e. l vs σ_a)

- Advantages
  - Stable
  - Reliable crack path
  - Sample does not split apart
  - Crack faces remain matched



Fracture Testing

- 2MEP4FS DMA sample repurposed for DCDC testing

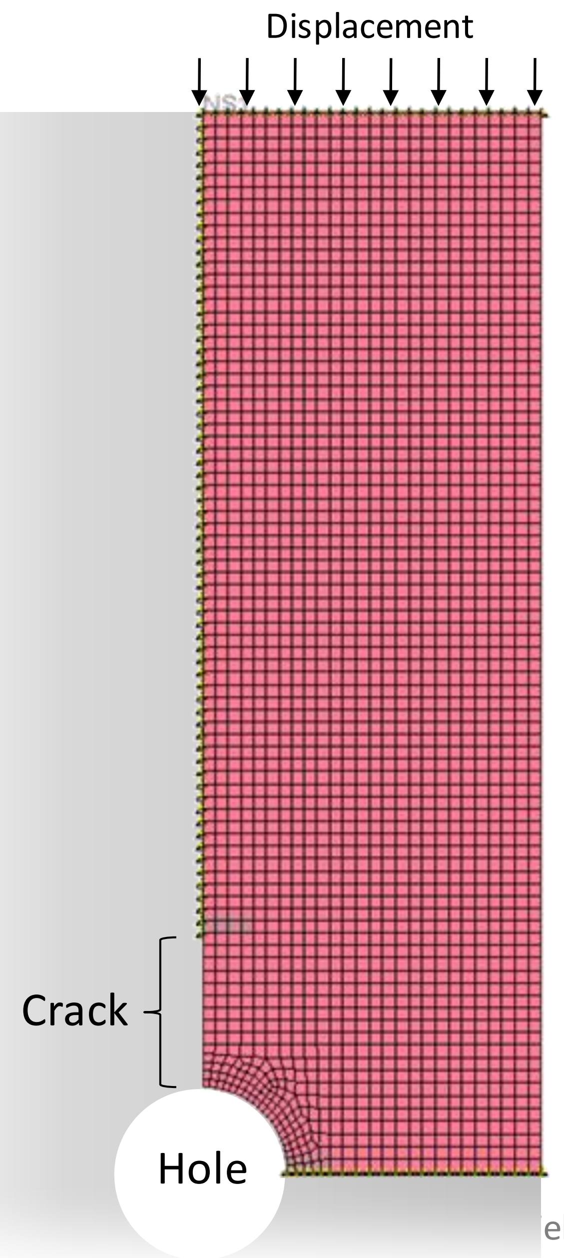


Modeling the DCDC Test

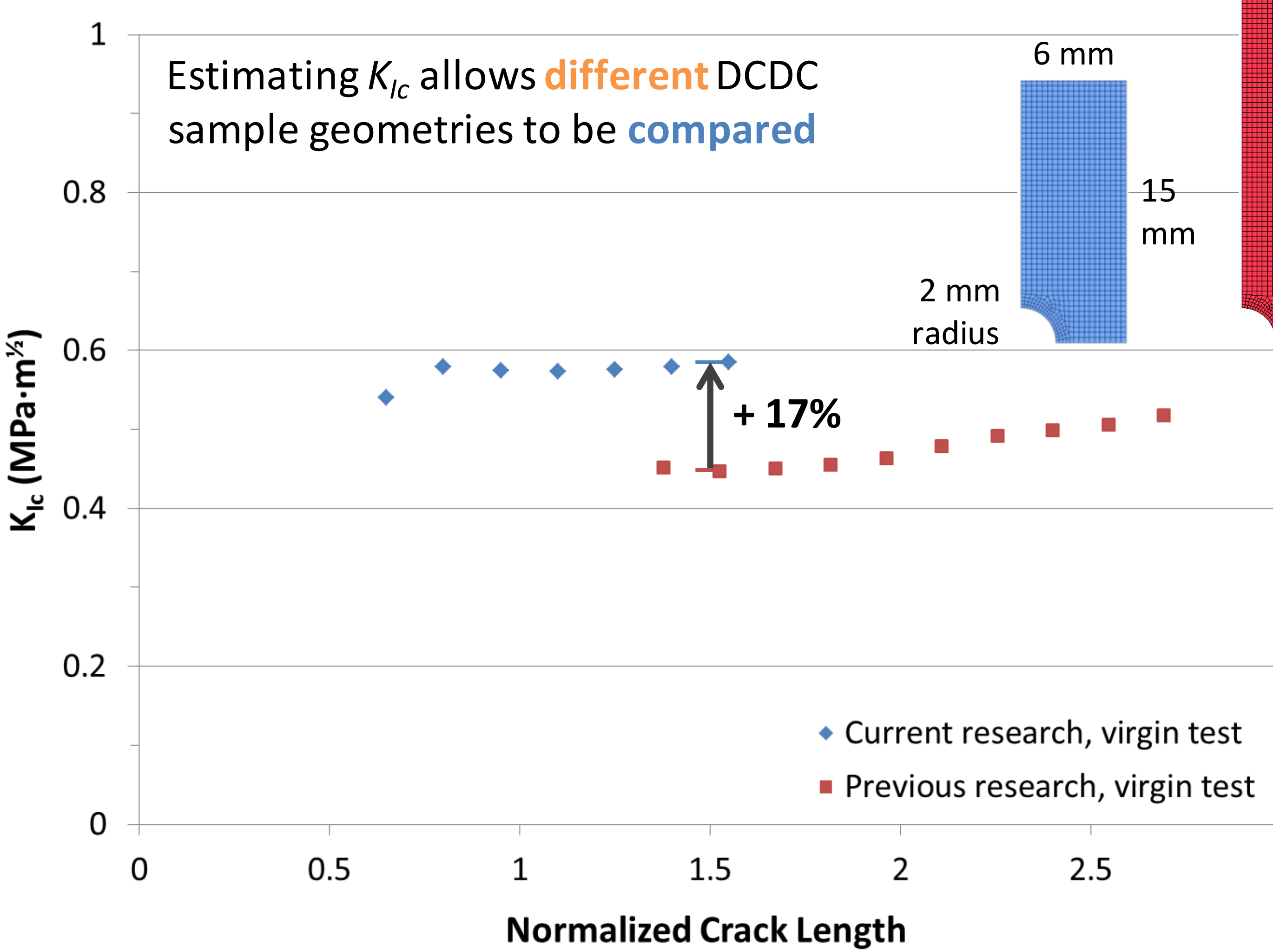
- 2D, one-quarter model with appropriate boundary conditions
  - LS-DYNA implicit
  - Plane stress shell elements
  - Elastic isotropic material

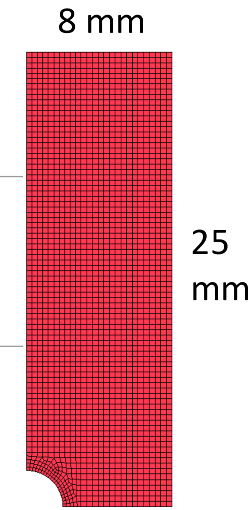
- Crack grown by releasing boundary conditions in **sequential models**

- Simulation crack lengths & forces **correlated with experimental results**
  - Energy release rate, $G = -2\dfrac{\Delta U}{\Delta l}$
  - Critical stress intensity, $K_{Ic} = \sqrt{GI}$



DCDC Results

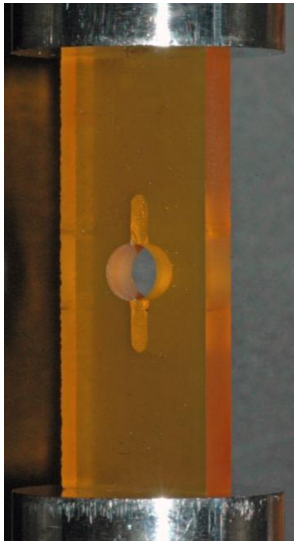




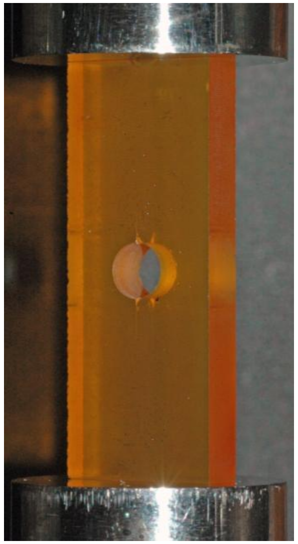
Fracture toughness of 2MEP4FS polymer has *improved*

Healing

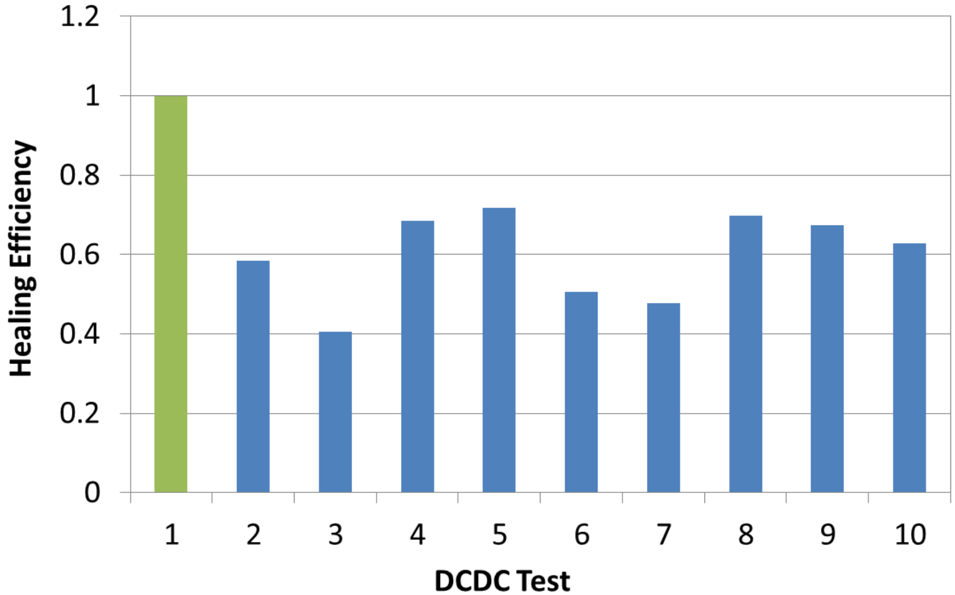
- DCDC cracks were healed and the sample was retested



Fractured



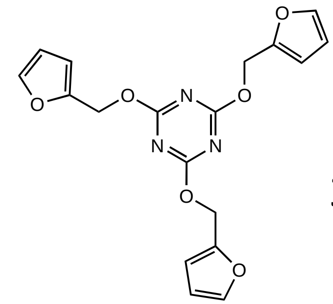
Healed



- Incomplete crack healing **due to sample geometry**
- Efforts to test the material using the previous sample geometry are ongoing

Other Healable Polymers

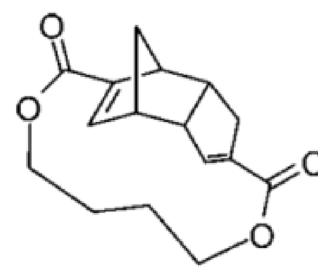
- 2MEP3FT
  - Modified diene monomer replaces 4FS
  - New polymer did **not demonstrate** presence of thermally reversible bonds



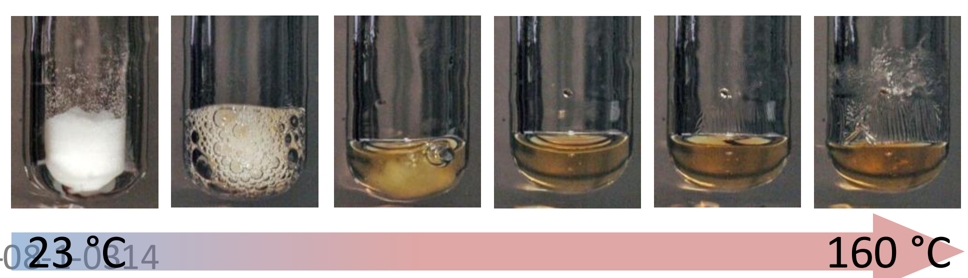
3FT

↘ Collaboration with Dr. Haim Weizman (UCSD Chem. Dept.)

- Mendomer 400
  - Single component monomer with both diene and dienophile functional groups
  - **Limited quantity** precluded mechanical testing



Monomer 400

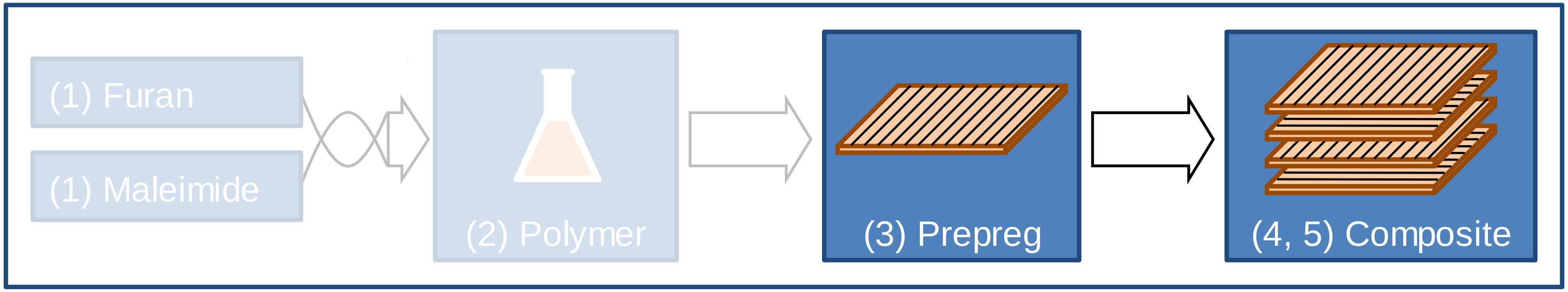


↘ Collaboration with Dr. Terrisa Duenas (NextGen Aeronautics)

NextGen Aeronautics
Inventing Technologies for the Next 100 Years of Flight

Research Outline

1. Process polymer components: furan and maleimide monomers
2. Characterize neat polymer (mechanical, thermal and crack healing properties)
3. Develop pre-preg system of oriented fibers and healable polymer matrix
4. Laminate pre-preg layers to form composite panels with minimal voids & defects
5. Characterize the composites: determine mechanical and crack healing properties



Challenges

- At room temperature, 2MEP is **solid** and 4FS is a **viscous liquid**
- Raising the temperature to 90°C melts 2MEP and reduces viscosity, but polymerization occurs within **a couple minutes** leaving little time for distribution among fibers

2MEP

4FS

Challenges

Healable polymer → Healable composite

- Injection process: **one** step

Monomer mixing, fiber integration and polymerization

- Pre-preg process: **separate** steps

Monomer mixing › Fiber integration › Polymerization

Pre-preg Advantages

Monomer mixing › Fiber integration › Polymerization

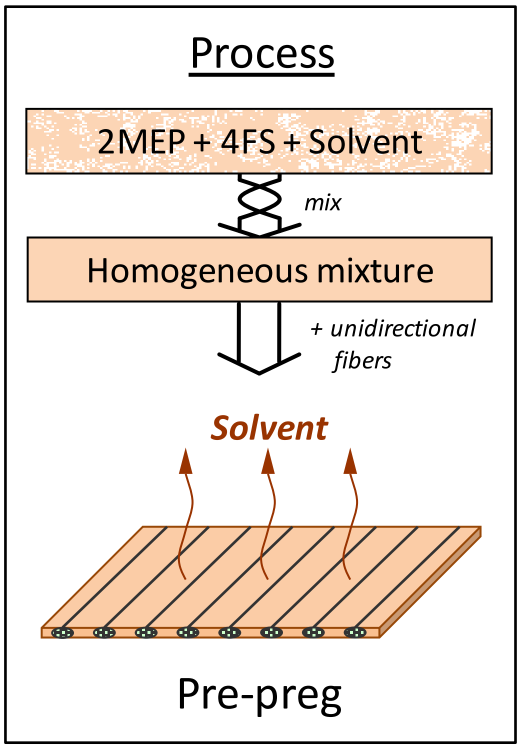
- **Flexible** – after each step, the result can be stored for later use
- **Adaptable** – Custom composite structures can be fabricated from multiple pre-preg layers

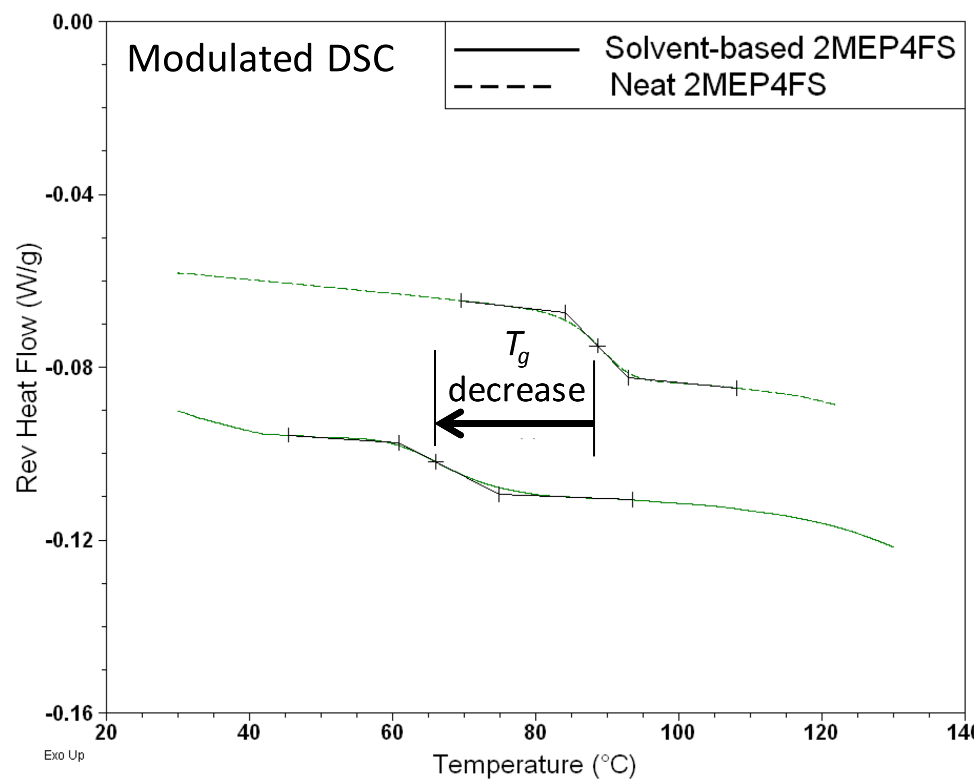
Objective

- Create a pre-preg system for building healable composites

Pre-preg Approach #1

- Use a **solvent** to mix monomers and facilitate distribution in a thin layer of fibers
  - Thin cross-section and large surface area aids solvent removal

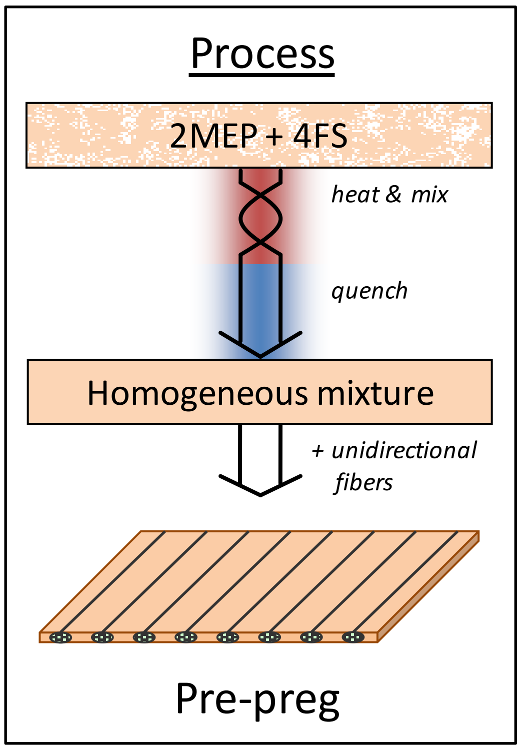


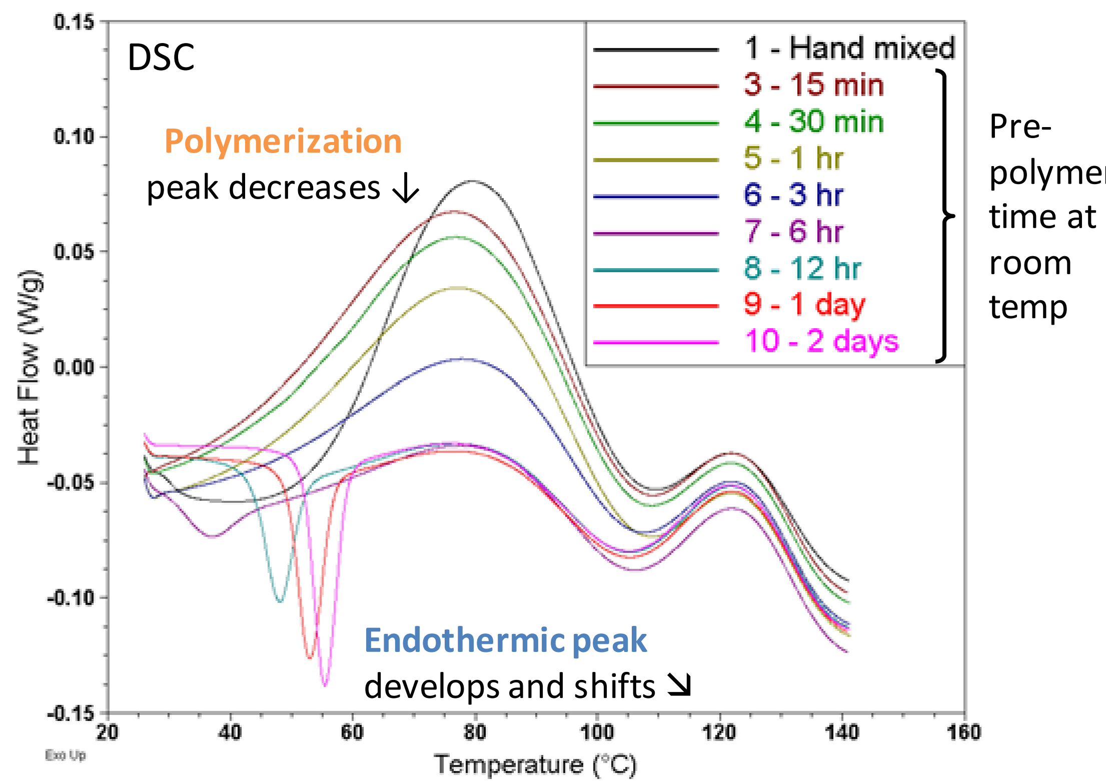


Trace amounts of solvent significantly affect 2MEP4FS properties

Pre-preg Approach #2

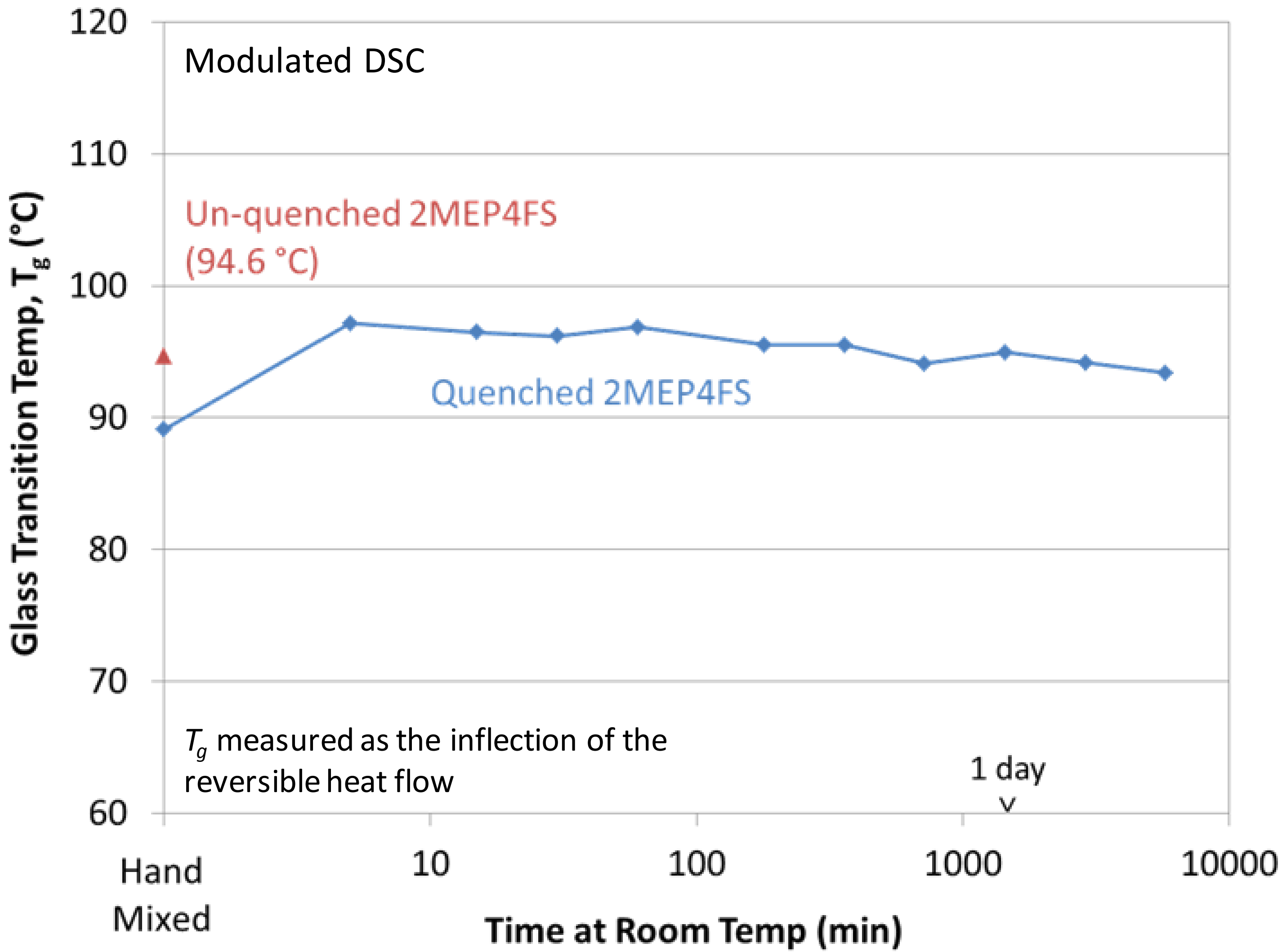
- Make pre-preg without solvent by **slowing the polymerization** to allow time for distribution
  - Spread pre-polymer among fibers





Polymerization can be completed during composite lamination

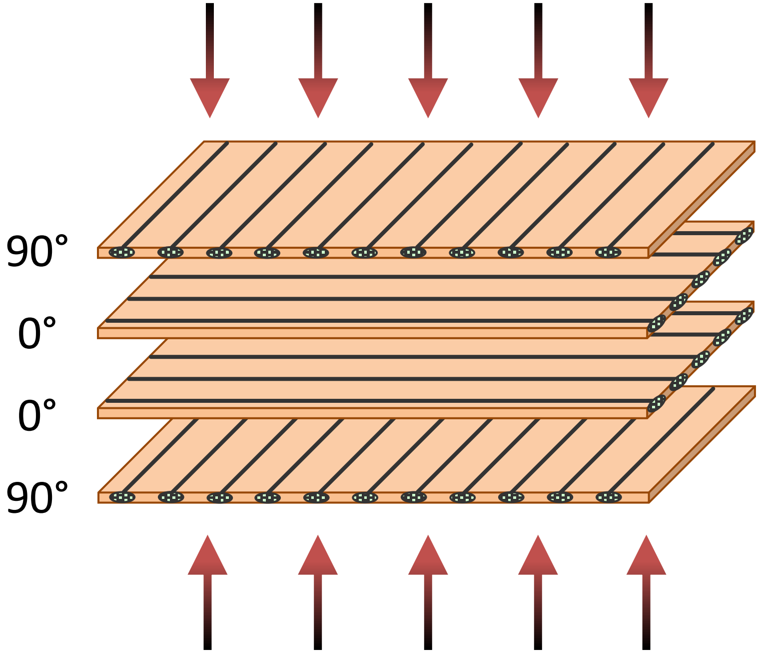
Cured 2MEP4FS



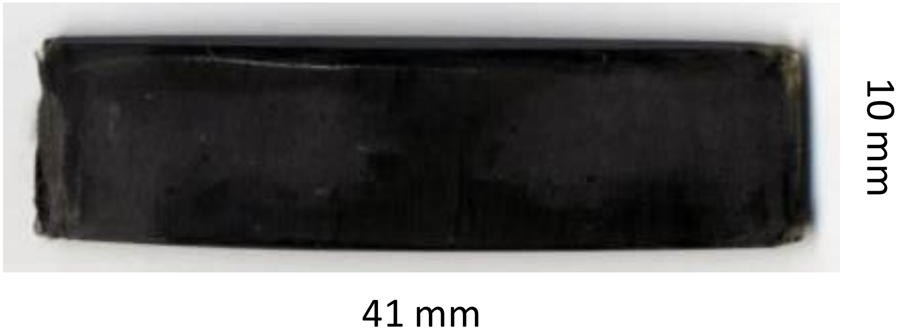
T_g of cured 2MEP4FS minimally affected by time at room temp

Multi-layered Composite

- Pre-preg: 2MEP4FS pre-polymer combined with unidirectional carbon fiber
- Four layers laminated to form $[90,0]_s$ composite



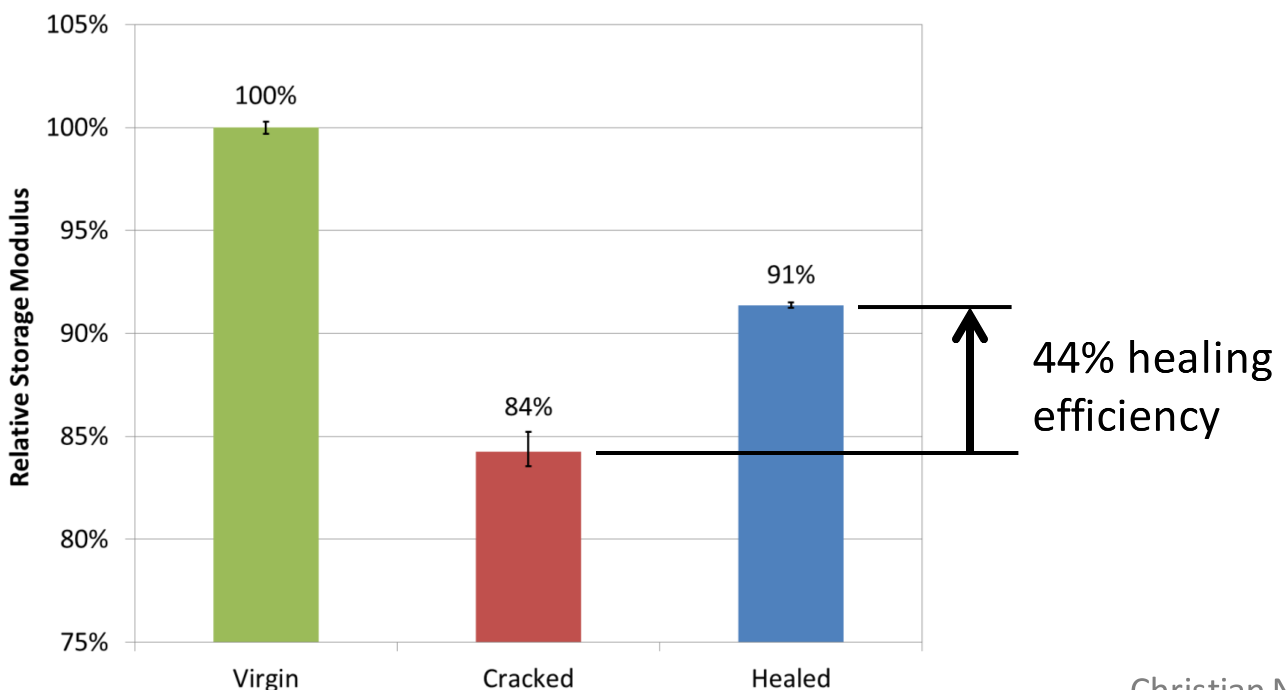
Top view of $[90,0]_s$ healable composite



Fiber volume fraction, $V_f \approx 20$ %

Multi-layered Composite

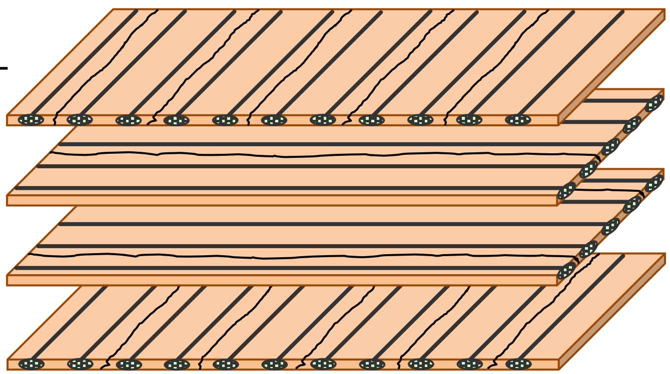
- DMA used to characterize composite:
  - in virgin state (**Green**)
  - after 5 thermal cycles in liquid nitrogen (**Red**)
  - after 2 hours at 100 °C (**Blue**)

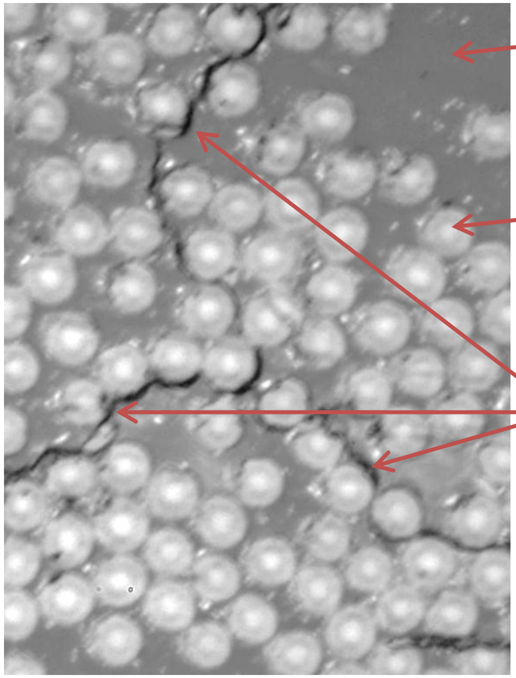


Multi-layered Composite

- Crack healing method relied on **thermal expansion** to close cracks in 90° plies

CTE (μm/m/°C)
42
1
1
42
(estimated)





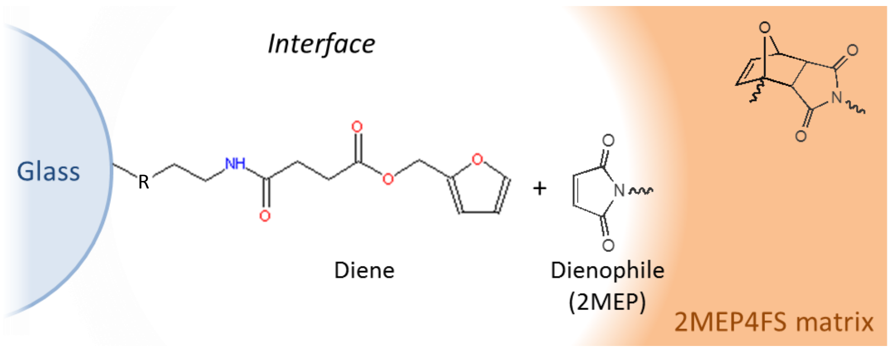
- Must **actively close cracks** to improve healing

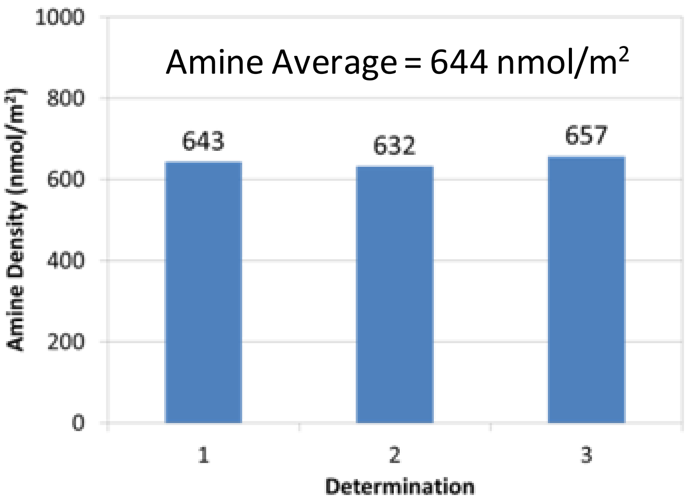
Functionalized Glass Fibers

- Create a healable fiber-matrix interface

  Peterson AM, Jensen RE, Palmese GP. Thermoreversible and remendable glass-polymer interface for fiber-reinforced composites. Comp Sci Tech 2011;71:586-92.

- First step: functionalize glass with amino (NH_2) groups
  - Picrate test†: Use acid-base interactions and UV spectroscopy to quantify amino groups





† Lee CCY, Loudon GM. Quantitative determination of amino groups on derivatized controlled pore glass: a comparison of methods. Anal Biochem 1979;94:60-4.

Summary

- Goal: Develop healable, fiber reinforced composites using a pre-preg approach
- Accomplishments:
  - Improved mechanical (E', K_{Ic}) and thermal properties (T_g) of 2MEP4FS
  - Critical stress intensity factor, K_{Ic}, estimated to be 0.5-0.6 MPa·m$^{1/2}$
  - Pre-preg layers fabricated and laminated to form a multi-layered composite
  - Glass fibers functionalized with known number of amino groups as the first step towards creating a healable interface
- Ongoing work:
  - Improve fracture/healing experiments of neat polymer and composite
  - Functionalize glass fibers and include in composite fracture healing studies

Acknowledgements

- Haim Weizman
  UCSD Chemistry Department
- Or Weizman
  High School intern, CEAM
- Eva Baylon
  Undergraduate intern, CEAM
- Dmitry Uchenik
  Chemistry Student, UCSD
- Yitzhak Tor
  UCSD Chemistry Department
- Alireza V. Amirkhizi
  Research Scientist, CEAM
- Jon Isaacs
  Sr Development Engineer, CEAM
- Tom Plaisted
  Army Research Lab
- Les Lee
  Air Force Office of Scientific Research

Research supported by AFOSR/ARO